THE PREPARATION OF PHENYLMALEIC ANHYDRIDE AND ITS APPLICATION TO THE DIENE SYNTHESIS

BY

DAVID JACOB MANN

B. S., Long Island University, 1941
M. S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Introduction

Phenylmaleic anhydride was first isolated by Alexander in 1890 (1) as a by-product in the preparation of the phenylmalic acids. The yield of phenylmaleic anhydride was low and, consequently, this procedure was unsuitable as a preparative method for phenylmaleic anhydride in relatively large quantities. No other method of preparation has been reported since that time.

The reaction of phenylmaleic anhydride in a Diels-Alder reaction has not been reported previously.

The purpose of the present investigation was to develop a new method for the preparation of phenylmaleic anhydride and to determine whether phenylmaleic anhydride would participate in the Diels-Alder diene reaction.

Discussion of Results

When phenylsuccinic anhydride (2) was permitted to react with N-bromosuccinimide in the presence of a catalytic amount of benzoyl peroxide, phenylmaleic anhydride could be isolated in 56-64% yield depending upon the amounts of reactants used.

That phenylmaleic anhydride does participate in a Diels-Alder reaction as a dienophile has been demonstrated by its adduct formation with anthracene, 2,3-dimethyl-1,3-butadiene, 1,3-butadiene, cyclopentadiene, isoprene, 2-ethyl-1,3-butadiene, and 2-isopropyl-1,3-butadiene. In the cases of the four symmetrical dienes only one product was isolated from each reaction mixture. The three unsymmetrical dienes on the other hand produced two products each, one of which was in great preponderance over the other. The

two products isolated in each of these cases were shown to be structurally isomeric rather than stereoisomeric in nature as was indicated by the degradation of both the isoprene and the 2-ethyl-1,3-butadiene adducts to the known *meta*- and *para*-phenylbenzoic acids (3,4). Although the degradation of the 2-isopropyl-1,3-butadiene adducts was not successful, they are assumed to be structurally isomeric on the basis of the structural similarity of the starting dienes.

That these adducts were not polymeric was shown by their physical and chemical properties and the rather close agreement of their neutral equivalents to the calculated values. The methyl esters of the adducts (except anthracene) have been prepared using an ethereal solution of diazomethane.

Phenylmaleic anhydride did not form an adduct with furan. When phenylmaleic anhydride was allowed to react with 2,3-dimethoxy-1,3-butadiene and with piperylene, a product was isolated in each case which could not be purified by recrystallization.

When phenylmaleic anhydride was allowed to react with 1-vinylnaphthalene using propionic acid as the solvent, two products were isolated; one in only small amount. While the product in predominant amount was shown to be a monomeric dibasic acid adduct by its elementary analysis and neutral equivalent, the product in small amount was shown to be an adduct anhydride by its elementary analysis and its insolubility in 5% aqueous sodium bicarbonate. That the dibasic acid adduct was a derivative of 1,2,3,4-tetrahydro-1,1′-binaphthyl was shown by its degradation to the known 1,1′-binaphthyl (5) by several different methods. Since, if phenylmaleic anhydride did act as a dienophile in this reaction, the resulting adduct with 1-vinylnapthalene should have been a derivative of either 1- or 2-phenyl-1,2,3,4-tetrahydrophenanthrene, it was considered important to establish rigidly the structure of the dibasic acid adduct. Towards this end, the adduct was degraded to 1,2,3,4-tetrahydro-1,1′-binaphthyl which was then compared with a sample of

1,2,3,4-tetrahydro-1,1′-binaphthyl prepared by an indepedent synthesis; both samples were found to be identical. Finally, the dibasic acid adduct was prepared by an independent method, and when compared with the original adduct diacid, the two were found to be identical. Thus, it has been established conclusively that phenylmaleic anhydride participates *as a diene* in a Diels-Alder reaction with 1-vinylnaphthalene.

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VITA

The author was born in Patchogue, New York, on November 6, 1919. He attended the public schools of Patchogue, New York, graduating from Patchogue High School in June, 1937. In the fall of that year he entered Long Island University from which he was graduated in June, 1941, with the degree of Bachelor of Science. He attended the Polytechnic Institute of Brooklyn in the fall of 1941, and was employed as a government inspector of powder and explosives from January, 1942, to June, 1942. From June, 1942, to February, 1946, he served in the Army of the United States. He entered the Graduate College of the University of Illinois in June, 1946, and received the degree of Master of Science in June, 1947. He held a part-time teaching assistantship from September, 1947, until February, 1950.